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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Cellular Polylactams

We, E. I. Du Pont De Nemours and Company, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the reinforcement of cellular polylactam articles.

It has long been desired, especially by the building and furniture industries, to use a satisfactory substitute for wood, particularly on account of the latter's dimensional sensitivity to moisture and lack of resistance to pests, rot and weathering generally. Plastics could overcome some, at least, of these disadvantages, and also can easily be shaped, e.g. by casting, and so are more suitable than wood for mass production and pre-fabrication, but in spite of all these apparent advantages, have not found commercial acceptance heretofore, since they are inherently expensive, especially such materials as polylactams. Foamed reinforced plastics, including polylactams, are generally volumetrically cheaper and lighter than unfoamed unreinforced plastics, but, heretofore have suffered from many of the same defects as wood, e.g. dimensional sensitivity to moisture, and have not, so far, found sufficient commercial acceptance in preference to wood and other prior art materials. In spite of many suggestions, therefore, there has existed for many years a very real practical problem of overcoming the inherent cost disadvantage of plastics without imparting to the plastic the disadvantageous characteristics of wood itself.

According to the present invention, there is provided a cellular polylactam article comprising a solids content of 10 to 80% by volume, 5 to 50%, preferably up to 30%, by weight of such solids being short fibers of inert material of modulus 5 to 30 x 10^6 psi, and of cross sectional dimension "D" 0.1 to 1 mil (2.5 to 25 microns) and length of from 3D to 125 mils (3.1 mm), preferably from 5D to 65 mils (1.6 mm), and wherein such fibers are dispersed substantially exclusively in the walls of the cells of the article, the long dimension being substantially parallel to the surface of the cell, more or less as shown, schematically, in the accompanying drawing. Generally, the shorter the fibers, the greater the amount that can be used conveniently, e.g. not more than 30% by weight of the solids are generally desirable if the fiber length is over 65 mils (1.6 mm).

The inert material of the short fibers may be, for example, calcium silicate, glass, slag wool and fibrous potassium titanate, such as have a modulus of substantially 8 to 10 x 10^6 psi aluminium, of modulus 10 to 11 x 10^6 psi, copper, of modulus 15 to 17 x 10^6 psi and steel, of modulus 27 to 30 x 10^6 psi.

Non-fibrous or particulate fillers may be used in addition, and in fact it is often desirable that 10 to 90%, preferably at least 50% (or up to 45% of the total solids), by weight of the total filler be non-fibrous for processing purposes, i.e. to off-set any tendency of the fibrous filler to settle, so long as the total filler content is not so high, e.g. more than 60% by weight, as to affect adversely the strength and toughness of the final product. Suitable non-fibrous fillers include, for example, calcium carbonate, alumina, aluminium or calcium silicate, Portland cement, titanium dioxide and other finely-divided materials.

Suitable polylactams may be prepared by conventional methods from omega-lactams containing six or more atoms in the lactam ring, including enantholactam, caprylolactam, decanolactam, and un-, do-, penta- and hexadecanolactam, methylcyclohexanone isoximes and cyclic hexamethylene adipamide in addition to the preferred caprolactam, which is readily available

[*Price*

commercially, and mixtures of lactams may be preferred for some purposes. There has been considerable prior art disclosure of suitable polymerization conditions, for example in U.S. Patent Specifications Nos. 3,017,391-2 and in earlier British Patent Specifications Nos. 955,917, 977,359, and 991,482, describing and claiming especially the use of suitable anionic catalyst/cocatalyst combinations and other polymerization conditions, but it is important, for the purposes of the present invention, if the proper fiber orientation is to be achieved, that the fibrous fillers be incorporated with the monomer before polymerization and foaming.

Thus, there is provided also, according to the present invention, a process for preparing a cellular polylactam article, comprising forming a mixture of molten monomeric omega-lactam, preferably caprolactam at a temperature of 140 to 160°C., an anionic polymerization catalyst and a cocatalyst therefor, a blowing agent, and short fibers of inert material as defined above, and forming the article by polymerization and foaming in a suitably-shaped mold, preferably mixing one monomer stream A containing anionic catalyst with a second monomer stream B containing cocatalyst and with the blowing agent and pouring into the mold at a temperature of 140 to 215°C., for caprolactam, until solidification occurs.

Conventional blowing agents may be used, e.g. chemically-stable volatile materials, such as hexane, and/or chemical blowing agents such as the substituted allylic azides.

The following Examples further illustrate the invention:

Example I

Stream (A) is prepared by dissolving the cocatalyst consisting of 1.3 grams of the polycarbonate of the 2,2-bis(4-hydroxyphenyl) propane and 3 milliliters of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid ß-lactone in 75 grams of essentially anhydrous e-caprolactam. This stream is heated to about 150°C. under a nitrogen atmosphere.

To prepare stream (B), 500 grams of essentially anhydrous caprolactam containing 2.07 mole per cent of sodium caprolactam and 11.5 grams of potassium stearate is heated to about 150°C. under a nitrogen atmosphere. 288 grams of a thoroughly-dried filler shown in Table I (corresponding to 33% by weight of the final cellular article) is then dispersed in stream (B). It will be noted that Runs 1 to 3, according to the invention, all contain at least 10% fibrous filler, and that, for comparative purposes, Controls A to C were run, there being no filler at all in Control C, and only non-fibrous filler in Controls A and B.

The two streams, along with 12.1 milliliters of the blowing agent composed of equal parts by weight of dodecenylazide and hexane, are mixed and the resulting mixture is poured into an open-top mold (about 0.6 x 40 x 40 cm). The mold is held at 150°C. for about ten minutes and the resulting sheet is removed and tested for modulus, dimensional stability and thermal coefficient of expansion, the results being in Table I. The density of all the filled cellular articles is about 0.73 grams/milliliter.

The modulus is measured at 23°C. and at 50% RH according to A.S.T.M. D-790, and the thermal coefficient of expansion according to A.S.T.M. D-969-44. The dimensional stability is determined at 100% RH by cutting 1.25 x 8.75 mm samples from the sheet, weighing them and measuring their length accurately, before exposing them to three alternating wet-dry cycles, by immersion in boiling water for 20 hours, followed by drying at 120°C. in a continually-purged nitrogen atmosphere for 20 hours. Since the first cycle is quite sensitive to extraneous factors, e.g. the extractable content and molded-in stresses, the dimensional stability is given as the average length change (percentage of the original length) for the last two wet-dry cycles.

TABLE I

Run	Wt. % Filler: Fibrous	Wt. % Filler: Non-Fibrous	Modulus	Dimensional Stability	Thermal Coefficient Expansion
1	10 (a)	23 (c)	181,000	1.1	5.1×10^{-5}
2	10 (e)	23 (c)	152,000	1.1	5×10^{-5}
3	33 (b)	—	171,000	1.0	4.7×10^{-5}
A	—	10 (d) 23 (c)	117,000	2.1	8×10^{-5}
B	—	33 (d)	106,000	2.1	9.4×10^{-5}
C	—	—	62,000	2.7	11×10^{-5}

(a) " Cab-O-Lite " F-1-Wollastonite (calcium silicate) ore ground to yield fibres, longest being about 1.6 mm, and the lengths averaging 14 " D," manufacture by Cabot Corp.

(b) Milled glass fibres cut to lengths no greater than about 1.6 mm, and the length being about 3 " D," manufactured by Johns-Manville Co.

(c) Precipitated calcium carbonate, average particle size 7 microns, manufactured by Diamond Alkali Co.

(d) Tabular alumina, manufactured by Alcoa Corp.

(e) Glass fibres, length about 1.6 mm diameter about 10 microns manufactured by Owens-Corning Fiberglas Co.

EXAMPLE 2

The procedure of Example 1 is followed, except that 383 grams of the filler shown in Table II is dispersed in stream (B), to give a cellular article of density about 0.7 grams/milliliter, and 40% by weight of filler. By way of contrast, no fibrous filler is used in Control D.

TABLE II

Run	Weight % Filler: Fibrous	Weight % Filler: Non-fibrous	Modulus	Dimensional Stability
4	10 (a)	30 (f)	150,000	1.1
Control D	—	40 (f)	99,000	1.9

(f) " Glomax " WZ—A calcined clay, average particle size 7 microns, manufactured by Georgia Kaolin Co.

EXAMPLE 3

The procedure of Example 2 is followed, except that 7.6 milliliters of the blowing agent is used, to give a cellular article of density about 0.9 grams/milliliter, and the fillers in Table III are used. For comparative purposes in Control E, no fibrous filler is used.

TABLE III

Run	Weight % Filler		Modulus	Dimensional Stability
	Fibrous	Non-fibrous		
5	10 (a)	30 (f)	220,000	1.1
6	16 (a)	24 (f)	225,000	0.8
Control E	—	40 (f)	159,000	1.8

These comparative Examples show that the fibrous fillers, within the limitations indicated, significantly improve the modulus (stiffness) and dimensional stability to temperature and humidity changes of the foamed polylactam, without substantially reducing the basic toughness of the polylactam, in contrast to non-fibrous fillers.

Possible uses for the cellular articles of the invention include window and door frames, doors, shutters and drawers, e.g. for cabinets, especially such as are adaptable to mass production and pre-fabrication manufacture and/or assembly into houses or furniture.

WHAT WE CLAIM IS:—

1. A cellular polylactam article comprising a solids content of 10 to 80% by volume, 5 to 50% by weight of such solids being short fibers of inert material of modulus 5 to 30 x 10^6 psi, and of cross-sectional dimension "D" 0.1 to 1 mil and length of from 3D to 125 mils, and wherein such fibers are dispersed substantially exclusively in the walls of the cells of the article, the long dimension being substantially parallel to the surface of the cell.

2. An article according to Claim 1, wherein there are up to 30% of the weight of the solids of the short fibers.

3. An article according to Claim 1 or 2, wherein the length of the short fibers is at least 5D.

4. An article according to any of Claims 1 to 3, wherein the length of the short fibers is up to 65 mils.

5. An article according to any of the preceding claims, wherein at least some of the short fibers are calcium silicate fibers.

6. An article according to any of the preceding claims, wherein at least some of the short fibers are glass fibers.

7. An article according to any of the preceding claims, wherein at least some of the short fibers are slag wool fibers.

8. An article according to any of the preceding claims, wherein at least some of the short fibers are fibrous potassium titanate.

9. An article according to any of the preceding claims, wherein the short fibers are any of those hereinbefore specifically mentioned.

10. An article according to any of the preceding claims, wherein there is present also non-fibrous filler in amount such that the total filler content is not more than 60% by weight.

11. An article according to Claim 10, wherein the non-fibrous filler comprises up to 45% by weight of the article.

12. An article according to Claim 10 or 11, wherein the non-fibrous filler comprises at least 50% by weight of the total filler.

13. An article according to any of Claims 10 to 12, wherein at least some of the non-fibrous filler is calcium carbonate.

14. An article according to any of Claims 10 to 13, wherein at least some of the non-fibrous filler is alumina.

15. An article according to any of Claims 10 to 14, wherein at least some of the non-fibrous filler is aluminum silicate.

16. An article according to any of Claims 10 to 15, wherein at least some of the non-fibrous filler is calcium silicate.

17. An article according to any of Claims 10 to 16, wherein at least some of the non-fibrous filler is Portland cement.

18. An article according to any of Claims 10 to 17, wherein at least some of the non-fibrous filler is titanium dioxide.

19. An article according to any of the preceding claims, wherein at least some of the polylactam is polycaprolactam.

20. An article according to any of the preceding claims, wherein at least some of the polylactam is any of those hereinbefore specified.

21. A cellular polylactam article reinforced with short fibers oriented substantially as hereinbefore described with particular reference to the accompanying drawing.

22. A polylactam article according to Claim 21, substantially as described in any of the foregoing Examples.

23. A process for preparing a cellular polylactam article, comprising forming a mixture of molten monomeric omega-lactam, an anionic polymerization catalyst and a cocatalyst therefor, a blowing agent, and short fibers of inert material as defined in any of Claims 1 to 9, and forming the article by polymerization and foaming in a suitably-shaped mold.

24. A process according to Claim 22,

wherein there is also present in the mixture a non-fibrous filler as defined in any of Claims 10 to 18.

25. A process according to Claim 23 or 24, wherein at least some of the monomeric lactam is caprolactam.

26. A process according to Claim 25, wherein the temperature of the molten mixture is 140 to 160° C.

27. A process according to Claim 25 or 26, wherein the temperature of the mold is maintained at 140 to 125° C. until solidification occurs.

28. A process according to any of Claims 23 to 27, wherein at least some of the monomeric lactam is any of those hereinbefore specified.

29. A process according to any of Claims 23 to 28, wherein the blowing agent is a substituted allylic azide.

30. A process according to any of Claims 23 to 29, wherein the polymerization conditions are any of those specified in any of British Specifications Nos. 955,917, 977,359, and 991,482.

31. A process for preparing a cellular polylactam reinforced with short fibers substantially as hereinbefore described.

32. A process according to Claim 31, substantially as described in any of the foregoing Examples.

33. A cellular polylactam article prepared according to the process claimed in any of Claims 23 to 32.

34. An article according to any of Claims 1 to 22 or 33, in the form of a window shutter.

35. An article according to any of Claims 1 to 22 or 33, in the form of a window frame.

36. An article according to any of Claims 1 to 22 or 33, in the form of a window frame.

37. An article according to any of Claims 1 to 22 or 33, in the form of a door.

38. An article according to any of Claims 1 to 22 or 33, in the form of a drawer.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*